보건학석사 학위논문

Adsorption of benzalkonium chlorides (BACs) by powdered activated carbon (PAC)

분말 활성탄을 이용한 benzalkonium chlorides 흡착 제거에 대한 연구

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최 우 석

Abstract

Adsorption of benzalkonium chlorides (BACs) by powdered activated carbon (PAC)

Woo-seok Choe
Department of Environmental Health
Graduate School of Public Health
Seoul National University

Quaternary ammonium compounds (QACs) are cationic surfactants and are widely used for industrial products such as cosmetic and cleaning products. The most commonly used QACs are benzalkonium chlorides (BACs). Among BACs, benzyl dimethyl dodecyl ammonium chloride (BAC_{12}) that has 12 alkyl chain, benzyl dimethyl tetradecyl ammonium chloride (BAC_{14}) that has 14 alkyl chain, Benzyl dimethyl hexadecyl ammonium chloride (BAC_{16}) that has 16 alkyl chain are the most commonly used BACs. They have been utilized in many industries (food industries, textile industries, paper

industries, oil and gas industries, plastic industries, etc.) also to prevent biofouling in the pipelines and product deterioration. BACs are detected in the environment and are highly toxic even in small amounts. However, conventional water treatments are not being removed BACs well. Although it has been studied to reduce BACs by advanced oxidation processes or adsorption, some studies have been difficult to apply in real treatment plant. Therefore, in this study, we investigated the fundamental mechanism of major BACs adsorption to better understand the removal of major BACs in water treatment by using powdered activated carbon (PAC) that is commercial adsorbent in actual treatment plants and easy to apply. Adsorption experiments were carried out in batch form, and BACs were analysed by using HPLC-DAD. To investigate the adsorption characteristics of BACs using PAC, experiments were conducted at different concentrations, pH, temperature and dissolved organic matter. The adsorption difference between mixture of BACs and single BACs adsorption were also examined. BAC_{12}, BAC_{14} and BAC_{16} were adsorbed well on PAC and removal rates were more than 90 % within 20 minutes. The adsorption kinetic of BACs followed the pseudo-second order (q_e of 144.93-161.29 mg g^{-1} and k_2 of 3.18×10^{-3} -9.16×10^{-3} g mg^{-1} min^{-1}) and the isotherm was more suited to the Langmuir isotherm model (q_{max} = 188.68 -206.19 mg g^{-1}, K_L: 4.89-8.10 L mg^{-1}). Results of the adsorption experiments at various pH ranges, BACs removal from neutral and basic had more adsorption capacities than acid condition. Thermodynamic analyses examined that the adsorption BACs between PAC was spontaneous and endothermic reaction. In presence of dissolved organic matter in solution, BACs were complexed with humic acids and this complexed humic acids was adsorbed to PAC, resulting in increased BACs removal rate. Binary BACs experiments showed different characteristics compare to single BACs because their competed their

adsorption with each other. The adsorption capacities were reduced to 2.1-66.7 % compared to the BACs single adsorption. As a result of the adsorption of binary BACs, adsorption was increased in the order from BAC_{16}, BAC_{14}, BAC_{12}. The reason for the better adsorption of BAC_{16} was because van der Waals force is stronger due to more carbon chains than BAC_{12} and BAC_{14}. Our results imply that activated carbon can be a promising prospect in terms of removal efficiency of BACs.

Keywords: Adsorption, BACs, PAC, Kinetic, Isotherm, Binary solution

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1. Introduction

Quaternary ammonium compounds (QACs), are cationic surfactant compounds that have a positive charge nitrogen atom and linked at least one hydrophobic hydrocarbon chain. QACs are used in industrial products such as detergents, disinfectant products, preservatives, and pest control products (Ford et al., 2002). It is also used to remove the biofouling of the membrane that used in water treatment plant. The dose of QACs is used to prevent biofouling at a high concentration (300-1,000 mg L^{-1}) (Flemming and Geesey 2012). As QACs are used for many products, they are actually released into the environment. Annually About 75 % of the QACs consumed are discharged into wastewater treatment plants or directly to surface water (Ismail et al., 2010; Brycki et al., 2014).

There are several of types of QACs depending on what is connected to the nitrogen atom. There are 3 main structures of QACs; dialkyldimethyl ammonium compounds (DADMACs), alkyltrimethyl ammonium compounds (ATMACs) and benzalkonium chlorides (BACs) (Zhang et al., 2015). Among QACs, BACs especially alkyl chain lengths from C12 to C16 are the most commonly used and there are many studies that release into the environment (Tezel and Pavlostathis 2009). Table 2 shows the reported concentration of BAC in environment media. Besides, little dose of BACs can cause problem in the environment due to its strong toxicity. The toxicity of BACs is more toxic than other surfactant (Sütterlin et al., 2008). The ecotoxicity testing results for BACs are informed in Table 3.

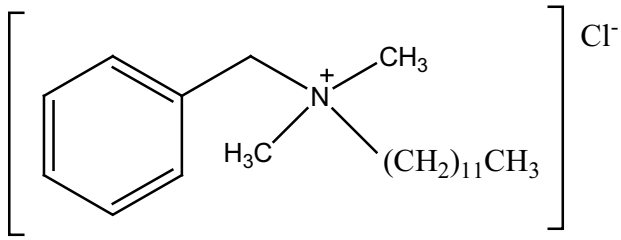
BACs is hardly removed during conventional treatment processes like sedimentation

and filtration. In Table 4, several studies have been reported recently to remove BACs. Especially, advanced oxidation processes (AOPs) widely studied to remove BACs like UV/chlorine, O_3/H_2O_2 and Fenton oxidation (H_2O_2/Fe^{2+}). (Huang et al., 2017; Khan et al., 2017a; Zhang et al., 2016). Other research used adsorption to remove BACs like municipal sludge, montmorillonite, natural clinoptilolite (Ismail et al., 2010; Ong et al., 2014; Farías et al., 2011). There are several studies to remove BACs, however some of the removal rate of BACs are poor or it need to be add lot of oxidizers to reduce BACs properly. Also there are some research that are difficult to apply in real situation, so it need to be apply easy process to real treatment plant.

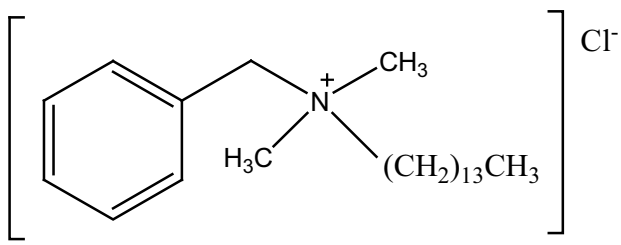
The most commonly process in water treatment plants is adsorption. The adsorption has very small pores on the surface, and the surface area per unit mass is very large. Using large surface area and van der Waals force removes the contaminants by physical adsorption. Adsorption use various kinds of adsorbents such as activated carbon, silica gel, and zeolite. Among adsorbents, activated carbon is the commercial adsorbent in water treatment plants. Advantages of activated carbon are that the treatment is simple and have high treatment efficiency (Gupta et al., 2009). Among the activated carbon, powdered activated carbon (PAC) is used in the actual treatment plant, especially for organic matters and micropollutants such as pharmaceuticals and biocides (Margot et al., 2013). Table 5 shows the products removal of the adsorption by PAC. In Table 5, various chemicals (micropollutant, dye, heavy metal) are removed well by PAC. Among micropollutants, substances such as sulfamethoxazole are not easily removed, but carbamazepine, propranolol and nonylphenol, which are composed mainly of carbon and have many benzyl

groups, are easily removed from the PAC. Therefore, it is considered that BAC consisting of carbon-rich alkyl group and benzyl group can be removed by PAC. Besides, adsorption study using activated carbon was not been conducted much, and adsorption characteristics of BACs by using PAC have not been elucidated.

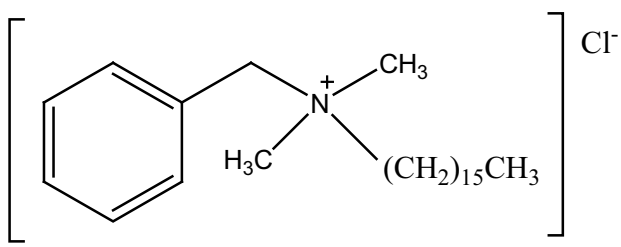
The objectives of this study were: (1) To examine the removal of benzalkonium chlorides that three mostly used (Benzyl dimethyl dodecyl ammonium chloride (BAC_{12}) and benzyl dimethyl tetradecyl ammonium chloride (BAC_{14}) and benzyl dimethyl hexadecyl ammonium chloride (BAC_{16})) by PAC; (2) To determine the adsorption kinetics and isotherms of activated carbon in various conditions (contact time, pH, temperature, dissolved organic matter) and (3) To compare removal of 3 different benzalkonium chlorides by PAC



(a) BAC_{12}



(b) BAC_{14}



(c) BAC_{16}

Figure 1. Molecular structures of BACs

Table 1 Characteristics of BACs substances

Substance	BAC_{12}	BAC_{14}	BAC_{16}
CAS No.	139-07-1	139-08-2	122-18-9
Molecular formula	$C_{21}H_{38}NCl$	$C_{23}H_{42}NCl$	$C_{25}H_{46}NCl$
Molecular weight	339.99	368.04	396.09
log K_{OW}[a]	2.93	3.91	4.89

BAC_{12} : Benzyl dimethyl dodecyl ammonium chloride
BAC_{14} : Benzyl dimethyl tetradecyl ammonium chloride
BAC_{16} : Benzyl dimethyl hexadecyl ammonium chloride
a: Zhu et al., 2010

Table 2 Occurrence of BACs in various environment media

Country	Media	BACs concentration	Reference
Europe	Hospital wastewater	0.05-6.03 mg L^{-1}	(Kümmerer et al., 1997)
Austria	Effluent WWTP	2.1-4.1 μg L^{-1}	(Kreuzinger et al., 2007)
Australia	Influent WWTP	25-300 μg L^{-1}	(Martínez-Carballo et al., 2007b)
United States	Urban estuarine sediment	18-74 ppm	(Li and Brownawell 2010)
China	River sediment	0.05-1.1 mg kg^{-1}	(Li et al., 2014)
China	Sludge	0.94-191 ppm	(Ruan et al., 2014)
China	Surface water	0.07-65 μg L^{-1}	(Zhang et al., 2015)
Korea	Soil	0.005-28.5 mg kg^{-1}	(Kang and Shin 2016)

Table 3 Comparison of ecotoxicity results for BACs

Compound	Species	End point	Concentration	Reference
BACs[a]	P. *subcapitata*	EC50 (72hr)	0.041 mg L^{-1}	(Kreuzinger et al., 2007)
BACs[a]	D. *magna*	EC50 (48hr)	0.041 mg L^{-1}	
BAC_{12}	C. *vulgaris*	EC50 (96hr)	0.203 mg L^{-1}	(Zhu et al., 2010)
BAC_{14}	C. *vulgaris*	EC50 (96hr)	0.174 mg L^{-1}	
BAC_{16}	C. *vulgaris*	EC50 (96hr)	0.160 mg L^{-1}	
BAC_{12}	D. *magna*	EC50 (48hr)	0.023 mg L^{-1}	(Chen et al., 2014)
BACs[b]	D. *magna*	EC50 (48hr)	0.038 mg L^{-1}	(Lavorgna et al., 2016)
BACs[b]	C.*dubia*	LC50 (24hr)	0.404 mg L^{-1}	
BAC_{12}	*Aliivibrio fischeri*	IC50	0.17±0.03 mg L^{-1}	(Di Nica et al., 2017)

BACs: Benzalkonium chlorides
BAC_{12} : Benzyl dimethyl dodecyl ammonium chloride
BAC_{14} : Benzyl dimethyl tetradecyl ammonium chloride
BAC_{16} : Benzyl dimethyl hexadecyl ammonium chloride
EC50 : Effective concentration 50 %
LC50 : Lethal concentration 50 %
IC50 : Inhibitory concentration 50 %
a: BAC_{12} : 60 %, BAC_{14} : 40 %, BAC_{16} <1 %
b: C_8H_{17} to $C_{18}H_{37}$

Table 4 Summary of BACs removal by various methods

Method	Dosage	Initial concentration	Removal rates	Reference
Fenton oxidation (H_2O_2/Fe^{2+})	H_2O_2 : Fe^{2+} = 8 mM : 0.8 mM	100 mg L^{-1}	79 %	(Zhang et al., 2016)
UV/Chlorine	Chlorine : 0-150 mg L^{-1}	100 mg L^{-1}	56.6-81.4 %	(Huang et al., 2017)
O_3/H_2O_2	Ozone : 1.28g h^{-1} H_2O_2 : 200 mg L^{-1}	75 mg L^{-1}	90 %	(Khan et al., 2017a)
Municipal sludge	1 g L^{-1}	300 mg L^{-1}	67-89 %	(Ismail et al., 2010)
Montmorillonite	1 g L^{-1}	72 mg L^{-1}	-	(Ong et al., 2014)
Agricultural soils	0.67-3.3 g L^{-1}	100 mg L^{-1}	20-80 %	(Khan et al., 2017b)

Table 5 Removal rate of various chemicals by PAC

Products	Chemicals	Removal rate (%)	Reference
PPCPs	Bisphenol A	31-99	(Yoon et al., 2003)
PPCPs	Nonylphenol	> 94	(Hernández-Leal et al., 2011)
PPCPs	Sulfamethoxazole	2-62	(Kovalova et al., 2013)
PPCPs	Propranolol	91-94	
PPCPs	Benzotriazole	69-94	
PPCPs	Carbamazepine	98-100	
PPCPs	Bisphenol A	49-78	(Mailler et al., 2015)
PPCPs	Paraben	70-96	
Dye	Malachite green	80.7-98.4	(Wang et al., 2010)
Dye	Methylene blue	82-99	(Cherifi et al., 2013)
Heavy metal	Pb^{2+}	59.9-93.6	(Guo et al., 2010)
Heavy metal	Cr^{6+}	99.4	(Jung et al., 2013)

PPCPs : Pharmaceuticals and personal care products

2. Materials and methods

2.1. Chemicals

BAC_{12}, BAC_{14} and BAC_{16} were purchased from Sigma-Aldrich Co. Ltd., (USA). Sodium dihydrogenphosphate (NaH_2PO_4, Sigma-Aldrich Co. Ltd., USA), sodium phosphate dibasic (Na_2HPO_4, Kanto chemical Co. INC., Japan) and phosphoric acid (H_3PO_4, Sigma-Aldrich Co. Ltd., USA) were used as buffer solution in pH 4.0-8.5 and ammonia solution (NH_3, 28-30 % v/v, Samchun Co., Korea), ammonium chloride (NH_4Cl, Sigma-Aldrich Co. Ltd., USA) were used as buffer solution in pH 10. Humic acids (MP Bio Inc, Solon, OH) was used as dissolved organic matter (DOM) solution. Ammonia solution (NH_3 28~30 % v/v) and acetic acid (CH_3COOH, Sigma-Aldrich Co. Ltd., USA) were used as buffer solution in the mobile phase of BACs with HPLC and acetonitrile (ACN, JT Baker, USA) was also used as in the HPLC mobile phase solutions. All chemicals were used without purification and solutions were prepared with ultrapure water using Milli-Q water purification system (Millipore, USA).

PAC (Shinki Chemical, South Korea) was coconut shell-based and its characteristics are shown in Table 6. The surface charge of the PAC was measured using a Zeta analyzer (ELSZ-1000, Photal Otsuka Electronics, Japan). Surface area analyzer (ASAP 2420, Micrometrics, USA) was used with gaseous nitrogen for surface probing via the Brunauer–Emmett–Teller (BET) method to measure surface area, pore volume and pore size of PAC. Point of zero charge (pH_{pzc}) was analysed using the pH drift method (Nasiruddin Khan and

Sarwar 2007).

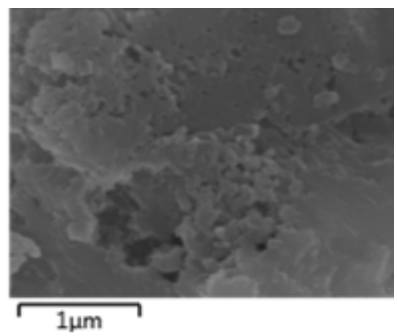


Figure 2. Scanning electron microscopy (SEM) image of PAC

Table 6 Characteristics of PAC

Adsorbent	PAC
Zeta potential (mV)	−26.49
Surface area (m^2 g^{-1})	945
Pore volume (cm^3 g^{-1})	0.52
Pore size (Å)	21.9
Bulk density (g cm^{-3})	0.5-0.8
Point of zero charge (pH_{pzc})	6.48

2.2. Experimental procedure

The experiments of BACs degradation were conducted by bench-scale and batch experiment using jar tester. PAC was washed several times with ultrapure water to remove the impurities before used. After washing with water, the mixture was filtered by using 0.45 μm membrane filter (ADVANTEC, Japan) to separate PAC from the water. Then PAC was dried at 80 °C for 12 hr in the oven. The experiment was carried out with 400 mL solution at 500 mL beaker was used. The initial concentration of BACs was 200 mg L^{-1} in the pH 7 using 0.01 M phosphoric buffer solution. PAC was injected into beaker at concentration of 1.2 g L^{-1} and then was shaken at 50 rpm. The temperature was maintained at 25 ± 1 °C and relative humidity was maintained at 50 ± 5 % by using thermostat (SYSTRONICS, DDC-400R). The adsorption reactor batch system is shown in Figure 3.

The adsorption capacity q_e (mg g^{-1}) was calculated according to Equation (1)

$$q_e = \frac{(C_0 - C_e) \times V}{M} \quad (1)$$

Where q_e represents the sorption capacity of BACs (mg g^{-1}), V is the volume of experiment solution (mL), M is the mass of PAC (g), C_0 and C_e are the initial and final concentration of BAC (mg L^{-1}), respectively.

To investigate the effect of pH was performed by different initial pH of BAC solutions. The initial pH of BAC solution was adjusted as pH 4 to 10 by using 0.01 M phosphate

buffer and 0.01 M ammonia buffer solution. To study the adsorption isotherms, adsorption experiments were conducted by injecting different initial BAC concentrations. The initial concentration of BAC in the solution was in the range of 200-450 mg L^{-1} at 25 °C. The initial PAC was set at 1.2 g L^{-1}, and the initial pH was set at pH 7. To investigate the effect of temperature was performed by different temperature condition (4, 25, 35 °C) and other conditions were the same. To investigate the effect of DOM, 10,000 mg L^{-1} of humic acids solution was made by adding humic acids in distilled water. Humic acids solution was spiked and mixed in phosphate buffer solution (adjusted to pH 7) to make 5, 10, 20 mg L^{-1} of DOM concentration. After that solution was passed through a 0.2 μm membrane filter (ADVANTEC, Japan) to remove the insoluble substances. TOC analyzer (Shimadzu, TOC-V) was used to confirm the concentration of DOM solution. 300 mg L^{-1} of BACs was added to the DOM solution and other conditions were the same. To find the effect of binary and ternary solution effect, adsorption experiments were conducted by using three binary BACs mixtures (BAC_{12} & BAC_{14}, BAC_{12} & BAC_{16}, BAC_{14} & BAC_{16} and BAC_{12} & BAC_{14} & BAC_{16}) and ternary BACs mixtures (BAC_{12}, BAC_{14} and BAC_{16}). The BACs mixture concentration was 200 mg L^{-1} respectively and another ratio of ternary solution was conducted by nature environment ratio of BACs. All samples were collected by 1 mL syringe (Korea vaccine Co., South Korea) and filtered through 0.2 μm membrane filter (ADVANTEC, Japan) before analysis.

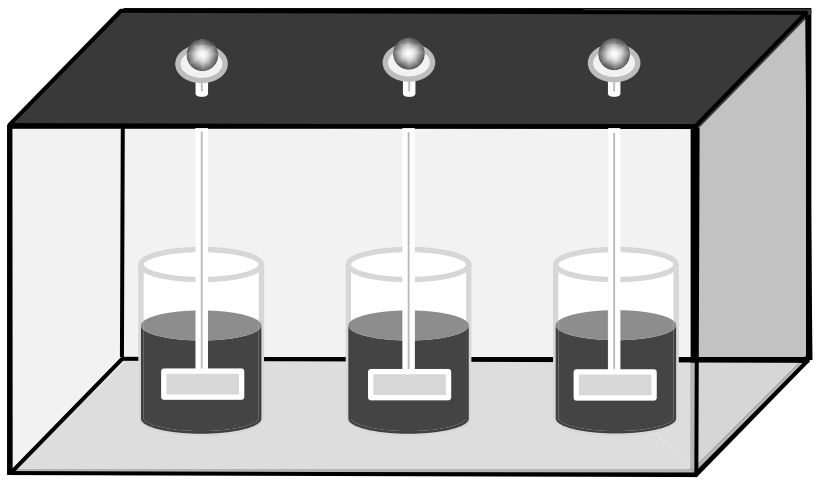


Figure 3. Schematic diagram of BACs adsorption experiment

2.3. Analytical method

Quantification of BACs was analyzed using a high performance liquid chromatography (HPLC) with a diode array UV detector (Dionex, DX-120). The column was a Luna® 5 μm C18 (phenomenex, 150 mm × 4.6 mm, 100 Å) and equipped with security guard column (phenomenex, 4 × 3.0 mm). The mode was isocratic mode and the mobile phase was a mixture of 80:20 (v/v) acetonitrile and 0.2 M ammonium acetate buffer solution (adjusted to pH 5 using H_3PO_4). Flow rate was 1.0 mL/min and injection volume was 100 μL and absorbance was 262 nm. Under these analytical conditions the run time was 18 min.

Quantification was performed using the external standard method based on several points (concentration range: 0.5-500 mg L^{-1}) calibration curve for individual BACs. As results, calibration curve correlation coefficient (R^2) of BAC_{12}, BAC_{14} and BAC_{16} showed higher than 0.99. It is obtained the limit of detection (LOD) of BACs calculating using calibration curve. The LOD of BAC_{12}, BAC_{14} and BAC_{16} were 0.26, 0.38 and 0.42 mg L^{-1} respectively.

3. Results and discussion

3.1. Kinetic studies

Adsorption kinetic studies of BACs to the PAC were conducted at 25 °C and the initial pH 7.0±0.1 by using phosphoric buffer solution. Equilibrium time of BAC adsorption was about 180 min. Figure 4 showed the removal of BAC_{12}, BAC_{14} and BAC_{16} by using PAC. Within the first 20 minutes, 90 % of BAC removal rate was removed. It observed higher BACs degradation than AOP studies (80 % removal rate after 1 hour) (Zhang et al., 2016). Figure 4 showed that BAC_{16} had higher degradation than BAC_{12} and BAC_{14}.

The results can be applied to two major kinetic models (pseudo-first order and pseudo-second order kinetic model) (Ho and McKay 1998; Rengaraj et al., 2004). The equation of pseudo-first order can be expressed as Equation (2), (3), (4):

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (2)$$

$$\int_0^{q_t} \frac{dq_t}{(q_e - q_t)} = \int_0^t k_1 dt \quad (3)$$

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \quad (4)$$

The equation of pseudo-second order can be expressed in linear form as follow

according to Equation (5), (6), (7):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (5)$$

$$\int_0^{q_t} \frac{dq_t}{(q_e - q_t)^2} = \int_0^t k_2 dt \quad (6)$$

$$\frac{\mathrm{t}}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

Where t (min) is the sampling time, q_e (mg g^{-1}) express the equilibrium amount of BAC adsorbed, q_t (mg g^{-1}) express the amount of BAC adsorbed at sampling time and it can be obtained in kinetic experiment. k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) are the rate constants of the pseudo-first order and pseudo-second order respectively. The slope and intercept can be obtained by linear regression of t against $\ln(q_e-q_t)$ and t against t/q_t. The rate constants of k_1, k_2 and q_e are obtained from the slope and the intercept.

The kinetic parameters including k_1 and k_2, calculated q_e values and the correlation coefficients (R^2) are given in Table 7. The R^2 values in the table show that the pseudo-second order is more appropriate than the pseudo-first order. The results of the Figure 4 and kinetic order in the Table 7 showed that the removal of BAC_{16} is higher than that of BAC_{12}, BAC_{14}. The reasons for the high removal of BAC_{16} are because of the increase of hydrophobicity and van der Waals interactions. The alkyl chain of BAC_{16} is longer than BAC_{12} and BAC_{14}, the hydrophobicity is increased and the van der Waals interaction would have more effect of each particles and PAC (Zanini et al., 2013).

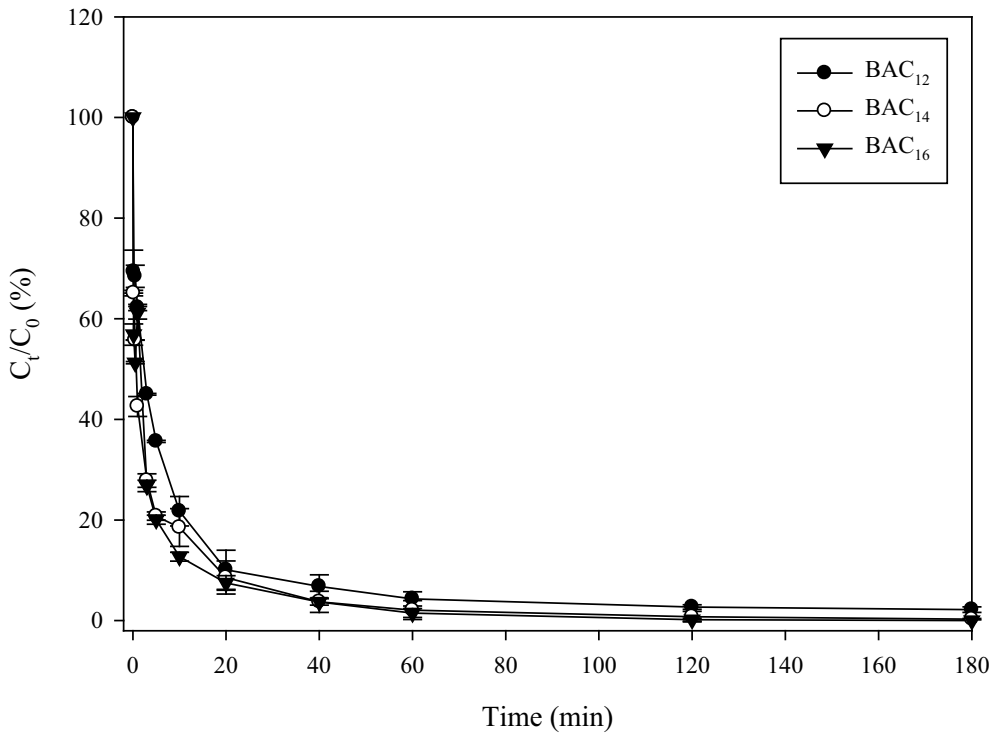


Figure 4. The degradation kinetics of BACs by adsorption of PAC ([C_0] = 200 mg L^{-1}; pH = 7.0 ± 0.1; temperature = 25 °C; contact time = 0–180 min; [PAC] = 1.2 g L^{-1})

Table 7 Parameters of pseudo first and second order of BACs on PAC ($[C_0]$ = 200 mg L^{-1}; pH = 7.0 ± 0.1; temperature = 25 °C; contact time = 0-180 min; [PAC] = 1.2 g L^{-1})

Models	BACs	Parameters	R^2
Pseudo-first order	BAC_{12}	q_e = 53.62 mg g^{-1} k_1 = 0.0601 min^{-1}	0.8346
	BAC_{14}	q_e = 64.08 mg g^{-1} k_1 = 0.0638 min^{-1}	0.8525
	BAC_{16}	q_e = 82.50 mg g^{-1} k_1 = 0.0665 min^{-1}	0.9473
Pseudo-second order	BAC_{12}	q_e = 144.93 mg g^{-1} k_2 = 0.00916 $gmg^{-1}min^{-1}$	0.9998
	BAC_{14}	q_e = 158.73 mg g^{-1} k_2 = 0.00620 $gmg^{-1}min^{-1}$	0.9996
	BAC_{16}	q_e = 161.29 mg g^{-1} k_2 = 0.00318 $gmg^{-1}min^{-1}$	0.9998

BAC_{12} : Benzyl dimethyl dodecyl ammonium chloride
BAC_{14} : Benzyl dimethyl tetradecyl ammonium chloride
BAC_{16} : Benzyl dimethyl hexadecyl ammonium chloride

3.2. Adsorption isotherms

The adsorption isotherms of BACs to the PAC were obtained from range 200-450 mg L^{-1} of BACs concentration over same amount of PAC (1.2 g L^{-1}) and the initial pH 7.0 and 25 °C. The adsorption parameters and correlation coefficients for BACs onto PAC obtained from 2 mainly isotherm models (Langmuir and Freundlich isotherms) (Caner et al., 2009).

Langmuir model represents the equilibrium distribution of ions between the solid and liquid phases (Dada et al., 2012). There are several assumptions of the Langmuir model; adsorbed molecules don't interfere with each other; adsorption occurs in the same mechanism; molecules adsorb to the adsorbent outer surface as a homogeneous (Ong et al., 2014). Homogeneous adsorption is that adsorbate adsorbs on the adsorbent and in equilibrium state no other adsorption can take in adsorbent (Foo and Hameed 2010).

The equation of Langmuir model can be expressed as follow (Equation (8), (9)):

$$q_e = q_{max} \frac{K_L C_e}{1 + K_L C_e} \quad (8)$$

$$\frac{C_e}{q_e} = \frac{1}{q_{max}} \times K_L + \frac{1}{q_{max}} \times C_e \quad (9)$$

Where K_L (L mg^{-1}) is Langmuir constants and q_{max} (mg g^{-1}) is maximum adsorption capacity. The slope and y intercept can be obtained by linear regression of C_e against C_e/q_e. The rate constants of K_L and q_0 are obtained from the slope and the intercept.

Freundlich model is commonly used to explain the adsorption for the heterogeneous surface. There is an assumption that adsorption occurs with a multilayer rather than a single layer (Fu et al., 2015). Heterogeneous adsorption is that adsorbate enters into the adsorbent and is adsorbed so that adsorption is continuously increased and adsorption equilibrium is not attained (Allen et al., 2004).

The equation of Fruendlich model can be expressed as follow (Equation (10), (11)):

$$q_e = K_F \times C_e^{1/n} \quad (10)$$

$$\log(q_e) = \log(K_F) + 1/n log(C_e) \quad (11)$$

Where K_F (L mg^{-1}) is Fruendlich constants and n is adsorption intensity. The slope and y intercept can be obtained by linear regression of $\ln(C_e)$ against $\ln(q_e)$. The rate constants of K_F and n are obtained from the slope and the intercept. The n value that is less than 1 indicates poor, 1-2 indicate moderately difficult, 2-10 indicate favorable and higher than 10 indicates non-reversible behavior of the adsorption isotherms (Ong et al., 2014).

The isotherm model parameters including K_L, q_{max} and K_F, calculated n values and the correlation coefficients (R^2) are showed in Table 8.

Table 8 Parameters of Langmuir and Freundlich model of BACs on PAC (pH = 7.0 ± 0.1; temperature = 25°C; contact time = 180 min; [PAC] = 1.2 g L^{-1})

Isotherm model	BACs	Parameters	R^2
Langmuir	BAC_{12}	q_{max} = 188.68 mg g^{-1}	0.9967
		K_L = 4.89 L mg^{-1}	
	BAC_{14}	q_{max} = 203.25 mg g^{-1}	0.9919
		K_L = 6.97 L mg^{-1}	
	BAC_{16}	q_{max} = 206.19 mg g^{-1}	0.9971
		K_L = 8.10 L mg^{-1}	
Freundlich	BAC_{12}	n = 21.41	0.8846
		K_F = 144.84 L mg^{-1}	
	BAC_{14}	n = 6.77	0.9491
		K_F = 119.84 L mg^{-1}	
	BAC_{16}	n = 15.33	0.8133
		K_F = 139.35 L mg^{-1}	

BAC_{12} : Benzyl dimethyl dodecyl ammonium chloride
BAC_{14} : Benzyl dimethyl tetradecyl ammonium chloride
BAC_{16} : Benzyl dimethyl hexadecyl ammonium chloride

Compared the correlation coefficients, the Langmuir model correlation coefficients value of the BAC_{12}, BAC_{14} and BAC_{16} were more than 0.99 and the value obtained by Freundlich model value of the BAC_{12}, BAC_{14} and BAC_{16} were 0.81-0.95. Through this result, the Langmuir model fitted better than Freundlich model due to homogenous distribution of active sites on the PAC surface, since the Langmuir equation assumes that the surface is homogenous (Alkan et al., 2004). Model and actual adsorption trend showed the BACs adsorption is homogeneous through the results of adsorption equilibrium was reached and the Langmuir model was fitted better than Freundlich model. Each coefficient of q_{max} of BACs showed that long alkyl chain such as BAC_{16} had more adsorption capacity.

In most of other articles, Langmuir model was suitable isotherm model for adsorption of BACs and their adsorption capacity (q_{max}) showed various values as various materials that was used by adsorbent. The lower than adsorption capacities of this article was 6.25-38.9 mg g^{-1} using agricultural soil; the adsorption capacities of BAC_{12} was 67 mg g^{-1} and BAC_{14} was 73 mg g^{-1} using sewage sludge (Khan et al., 2017b; Teresa García et al., 2006). The BACs adsorption capacities that higher than this research was using montmorillonite (334 mg g^{-1} for BAC_{12} and 448 mg g^{-1} for BAC_{14}) (Zanini et al., 2013). The common features of these articles are the long alkyl chain BAC had more adsorption capacities.

3.3. Effect of various pH on BACs adsorption

The effect of pH on BACs degradation by PAC adsorption was conducted at pH range 4 to 10 (4, 5.5, 7, 8.5, 10). The results of BAC adsorption capacities are showed in Figure 5. Figure 5 shows that the adsorption capacity increased from pH 4 to 7 and the adsorption capacity slightly decreased from pH 7 to 10. It indicated the highest adsorption capacity at pH 7.

As the pH changes, electrostatic interaction between the adsorbent and the contaminant can change. Electrostatic interaction has been the most widely applied to changes in organics adsorption, such as pharmaceutical and personal care products (Hasan et al., 2012; Sarker et al., 2017). In this study, BACs had ionized instantly in the solution forming cationic surfactant that not be affected by the pH (Ong et al., 2014). Therefore the surface of the PAC was changed rather than the BACs due to the pH change. If the pH is lower than pH_{pzc} of PAC, the adsorbent will have a positive charge, and if the pH is higher than pH_{pzc} of PAC, the adsorbent will have a negative charge. At pH 4 and 5.5, which were lower than pH_{pzc}, the charge of PAC was positive and it would have repulsion between positively charged BACs and PAC. Therefore at low pH, the adsorption capacities were decreased. At pH 7, 8.5, and 10, which were higher than pH_{pzc}, the adsorption capacities were higher than pH 4 and 5.5 because the surface of PAC was negative.

At pH 8.5 and 10, the surface of the adsorbent was negative, but the adsorption capacity was slightly decreased due to the form of hemi-micelle and micelle. High concentration of

surfactant could form hemi-micelle and micelle structure, and these forms adsorbed to the adsorbent (Rutland and Parker 1994; Atkin et al., 2003). When the pH is high, OH^- is attached to the positive on the surface of the micelle (Johnsson et al., 2003). And increased electrostatic repulsion between the negative charge surface of the PAC and BACs. Therefore, it had more adsorption capacity at pH 7 than pH 8.5 and 10.

However, PAC didn't have many functional groups for electrostatic forces, therefore van der Waals interaction was the main adsorption mechanism rather than electrostatic interaction. Figure 5 showed that BAC_{12} had more significant change in adsorption capacity than BAC_{14} and BAC_{16} according to pH change. The reason was that the number of alkyl chain increased, the effect of hydrophobicity increased rather than electrostatic interaction.

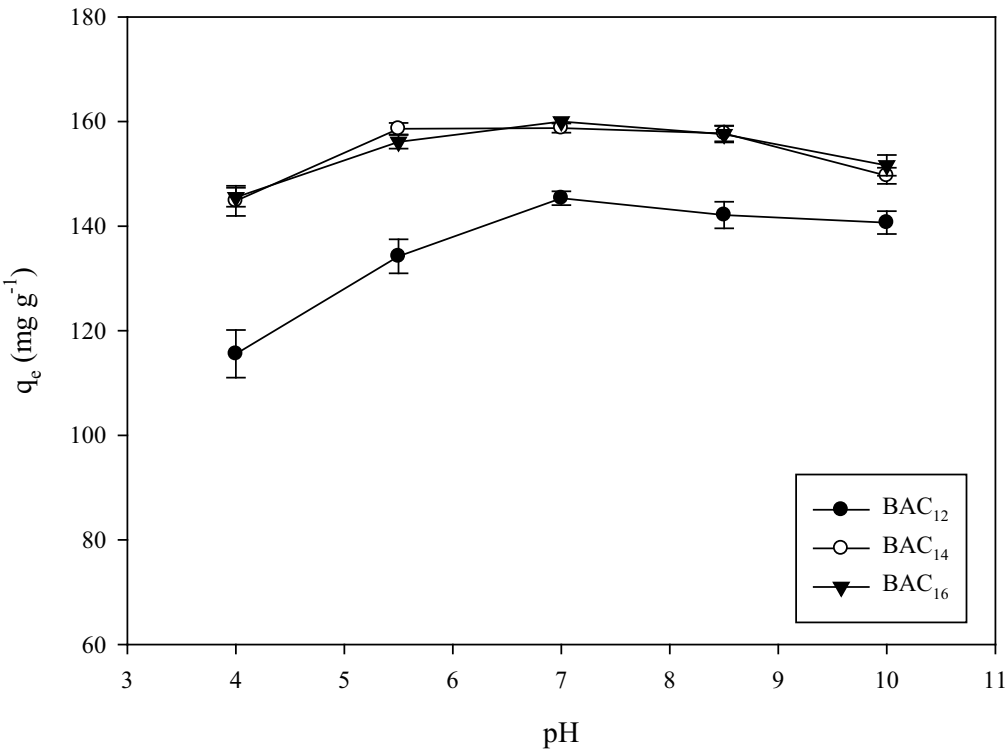


Figure 5. Effect of the initial pH on the adsorption of BACs ($[C_0]$ = 200 mg L^{-1}; temperature = 25 °C; contact time = 180 min; [PAC] = 1.2 g L^{-1})

3.4. Thermodynamic analyses

Temperature is an element that can occur in nature and is one of the factors that can affect adsorption. It can be known whether adsorption is exothermic or endothermic. In this study, adsorption experiments were carried out at different temperatures of 277, 298, and 308 K to observe the effect of temperature. Figure 6 shows that the q_{max} of BACs increased from 169.49-192.31 mg g^{-1} at 277 K to 232.56-264.62 mg g^{-1} at 308 K. Because the temperature increased, the BACs particles could move more actively and become more attached to the active surface site of adsorbent; and the adsorption reaction between PAC and BACs could be an endothermic reaction.

The van't Hoff equation was used to numerically determine whether the reaction was spontaneous or endothermic. Thermodynamic parameters including Gibb's free energy (ΔG^0, kJ mol^{-1}), standard enthalpy change (ΔH^0, kJ mol^{-1}), standard entropy change (ΔS^0, J $mol^{-1}K^{-1}$) were investigated by different temperature. Parameters can be determined using Langmuir isotherm by the following Equations (12), (13), (14):

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (12)$$

$$\Delta G^0 = -RTln(K_L) \quad (13)$$

$$\ln(K_L) = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (14)$$

Where R is the universal gas constant (8.314 J mol^{-1} K^{-1}) and T is the temperature (K). K_L is the distribution equilibrium coefficient (L mol^{-1}). ΔG^0 was obtained using K_L from the experiment. ΔS^0 and ΔH^0 were determined using slope and intercept from linear regression with $\ln(K_L)$ vs. 1/T value. The value of thermodynamic parameters are showed in Table 9.

The negative values of ΔG^0 showed that all the adsorption reaction occur spontaneously. The temperature was increased to 277 to 308 K, ΔG^0 more decreased so the reaction occur more spontaneously. Gas adsorption is normally ΔH^0 is negative (exothermic reaction) however in liquid adsorption ΔH^0 can be negative or positive value (Lowell et al., 2012). The positive values of ΔH^0 indicate the endothermic reaction of adsorption of BACs by PAC. Furthermore, the ΔH^0 value (1.000-3.571 kJ mol^{-1}) of BACs indicates that the adsorption process belongs to physisorption (i.e., ~20 kJ mol^{-1}) not chemisorption (i.e., 80-200 kJ mol^{-1}) (Ong et al., 2014).

Meanwhile, ΔS^0 usually become negative value in the case of adsorption of gases, because dispersed particles may be ordered arrangement on the adsorbent surface (Bhattacharyya and Sharma 2005). However in liquid system, results showed that ΔS^0 was positive values. The positive values of ΔS^0 explain the increasing randomness at the solid/liquid interface during the sorption of BACs on PAC (Boujelben et al., 2009). In water, the water molecules surround the BACs and become ordered structure. However the BACs are adsorbed to the adsorbent, the water molecules around the BACs are reduced and the degree of freedom of the water molecules is increased (Alkan et al., 2004). Other reason for increasing randomness is that PAC surface become more congested because large

molecules adsorbed on surface (Bhattacharyya and Sharma 2005). Therefore, ΔS^0 values could be increased when large molecules such as BACs were adsorbed at PAC.

BAC_{12}, BAC_{14} and BAC_{16} showed similar tendency. Besides other removal studies of heavy metals, dye and micropollutants using adsorbent of PAC have endothermic reaction with positive value of ΔS^0 (Rao et al., 2011; Liu et al., 2015; Suriyanon et al., 2013).

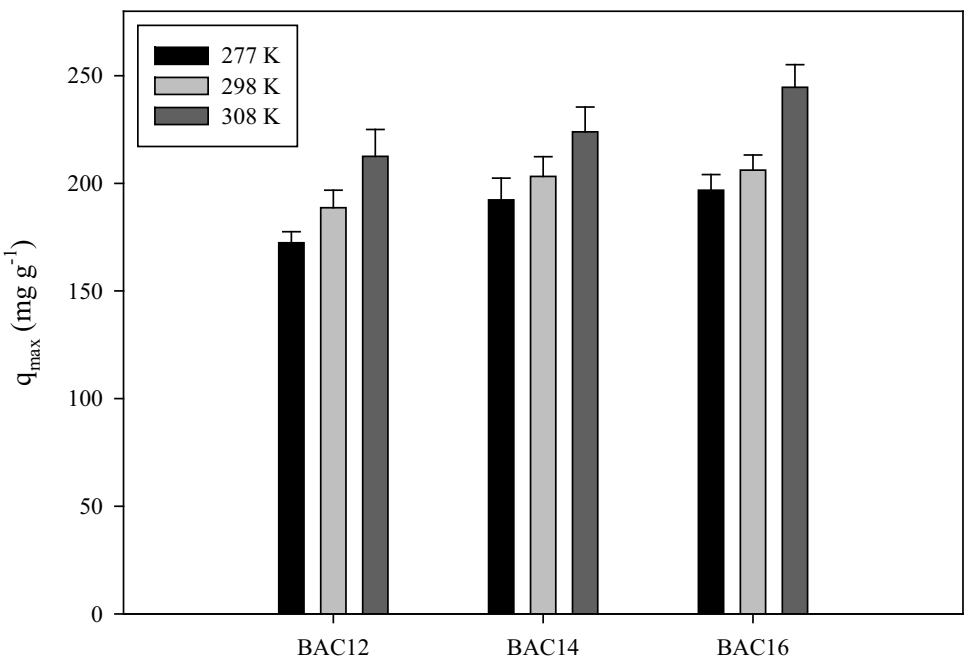


Figure 6. Effect of the temperature on the adsorption of BACs (pH = 7.0 ± 0.1; contact time = 180 min; [PAC] = 1.2 g L^{-1})

Table 9 Thermodynamic parameter for the adsorption of BACs

BACs	Temperature (K)	ΔG^0 (kJ mol^{-1})	ΔH^0 (kJ mol^{-1})	ΔS^0 (J mol^{-1} K^{-1})
BAC_{12}	277	-3.576	1.000	16.525
	298	-3.931		
	308	-4.085		
BAC_{14}	277	-4.276	3.497	28.020
	298	-4.811		
	308	-5.164		
BAC_{16}	277	-4.679	3.571	29.689
	298	-5.184		
	308	-5.641		

BAC_{12} : Benzyl dimethyl dodecyl ammonium chloride
BAC_{14} : Benzyl dimethyl tetradecyl ammonium chloride
BAC_{16} : Benzyl dimethyl hexadecyl ammonium chloride

3.5. Effect of DOM concentration on BACs adsorption

The DOM is naturally present in surface water and is released from the soil or from breakdown of plants and animals. DOM can range in molecular weight from 100 to 100,000 daltons with complex mixture of aromatic and aliphatic hydrocarbon structures that have attached amide, carboxyl, hydroxyl, ketone, and various minor functional groups. (Leenheer and Croué 2003). Most of DOM is humic substance (Weng et al., 2002). Therefore, humic acids solution was used in this research for DOM concentration. The effect of DOM on adsorption was conducted by different DOM concentration and DOM concentration was 0, 5, 10, 20 mg L^{-1} in solution.

In several research, adsorption efficiencies of heavy metals, PPCPs, dyes were generally reduced by presence of DOM (Wang et al., 2008; Behera et al., 2010; Murray and Örmeci 2017). Therefore, it was expected that the high concentration of DOM could be reduced the removal efficiency of BACs. The reasons of decreased adsorption rate are because direct competition between DOM and BACs on PAC and pore-blocking on adsorbent (Pelekani and Snoeyink 2000).

Figure 7 shows the results of effect of BACs removal rate at DOM exist and concentrations. The removal rates were 75.8-77.7 % at 0 mg L^{-1} of DOM concentration, 78.9-86.6 % at 5 mg L^{-1}, 81.7-95.2 % at 10 mg L^{-1} and 83.8-98.9 % at 20 mg L^{-1}. The removal rates of BACs were increased at 0 to 20 mg $L^{-1}$of DOM concentration. The reasons of opposite trend of several research are probably due to charge change and humic acids (HA)-complexed BACs. Some articles, humic acids behave like polyelectrolytes and have

negative charge so that when humic acids adsorb on the adsorbent, making surface negative charge (Newcombe 1994; Bjelopavlic et al., 1999). This change makes more adsorption of the BACs because its positive charge.

The log K_{OW} value of BAC_{12}, BAC_{14} and BAC_{16} are 2.93, 3.91 and 4.89, so it could be adsorb on the humic acids and have HA-complexed BACs (Behera et al., 2010). When complexed HA is adsorbed on PAC, it is similar result that BACs is adsorbed onto PAC surface. Therefore removal rate of BAC_{12}, BAC_{14} and BAC_{16} has been increased due to adsorb on both PAC and HA that attached onto PAC. Similar as this research, some studies showed presence of humic acid increased the removal rate of triclosan and dye (Behera et al., 2010; Murray and Örmeci 2017). In another study, the higher the log K_{OW}, the more adsorbed on humic acid and had more removal rate (Murphy et al., 1992). Therefore BAC_{12} in which log K_{OW} is lower than BAC_{14} and BAC_{16}, showed low increased removal rate in presence of DOM than BAC_{14} and BAC_{16}. As results of effect of DOM study, DOM in the water environment can increase removal rate by using PAC adsorption of BAC_{12}, BAC_{14} and BAC_{16} concentration in the surface water.

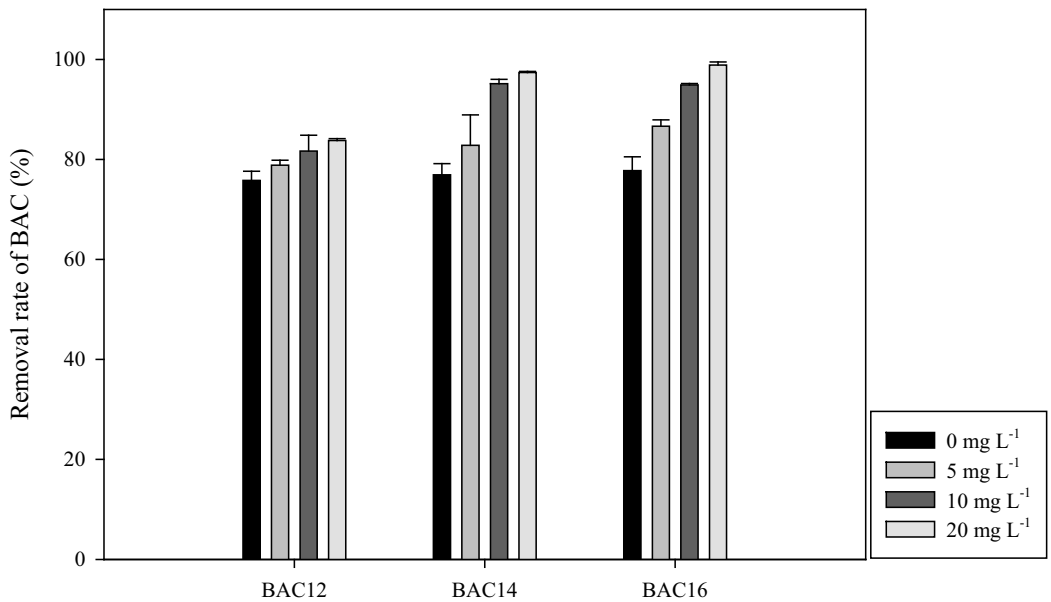


Figure 7. Comparison between DOM concentrations with BACs removal rate ($[C_0]$ = 300 mg L^{-1}; temperature = 25 °C; pH = 7.0 ± 0.1; contact time = 0–180 min; [PAC] = 1.2 g L^{-1})

3.6. Adsorption of binary and ternary BACs

BACs can be detected as a single substance in nature, however it can exist in more than two substances of BACs. There are studies in which two or more of BACs were detected in water and sediment (Ferrer and Furlong 2001; Martínez-Carballo et al., 2007a). If two or more BACs are in the solution, interaction may occur between them, and the adsorption reaction may be different from that of a single BACs. The results of binary adsorption were shown in Figure 8, 9, 10 and Table 10.

As shown in Table 10, PAC was affected by the presences of the other BACs in solution. BAC_{12} and BAC_{14} binary experiment result showed that BAC_{14} was more adsorbed to the PAC than BAC_{12} in the interaction of BAC_{12} and BAC_{14}. In the case of single experiment of BAC_{12}, it was 145.3 mg g^{-1} of adsorption capacity however decreased to 64.0 % in binary solution experiment. However in the case of BAC_{14}, it only decreased to 9.2 % in binary solution. BAC_{12} and BAC_{16} binary experiment result showed that the removal of BAC_{16} is better than BAC_{12}. In binary experiment, BAC_{16} decreased to 2.1 %, however BAC_{12} decreased to 66.7 % compared to single experiment result. BAC_{14} and BAC_{16} binary experiment result showed that BAC_{14} decreased to 48.3 %, and BAC_{16} decreased to 24.3 % compared to single BACs experiment.

Table 10 Adsorption capacity of BACs mixture

Mixture	BAC	Adsorption capacity ($mg\ g^{-1}$)		Adsorption difference (%)
		Single	Binary	
BAC_{12} & BAC_{14}	BAC_{12}	145.3	52.4	-64.0
	BAC_{14}	158.7	144.1	-9.2
BAC_{12} & BAC_{16}	BAC_{12}	145.3	48.5	-66.7
	BAC_{16}	160.0	156.6	-2.1
BAC_{14} & BAC_{16}	BAC_{14}	158.7	82.0	-48.3
	BAC_{16}	160.0	121.1	-24.3
BAC_{12} & BAC_{14} & BAC_{16}	BAC_{12}	145.3	34.8	-76.0
	BAC_{14}	158.7	76.1	-52.0
	BAC_{16}	160.0	111.2	-30.5

BAC_{12} : Benzyl dimethyl dodecyl ammonium chloride
BAC_{14} : Benzyl dimethyl tetradecyl ammonium chloride
BAC_{16} : Benzyl dimethyl hexadecyl ammonium chloride

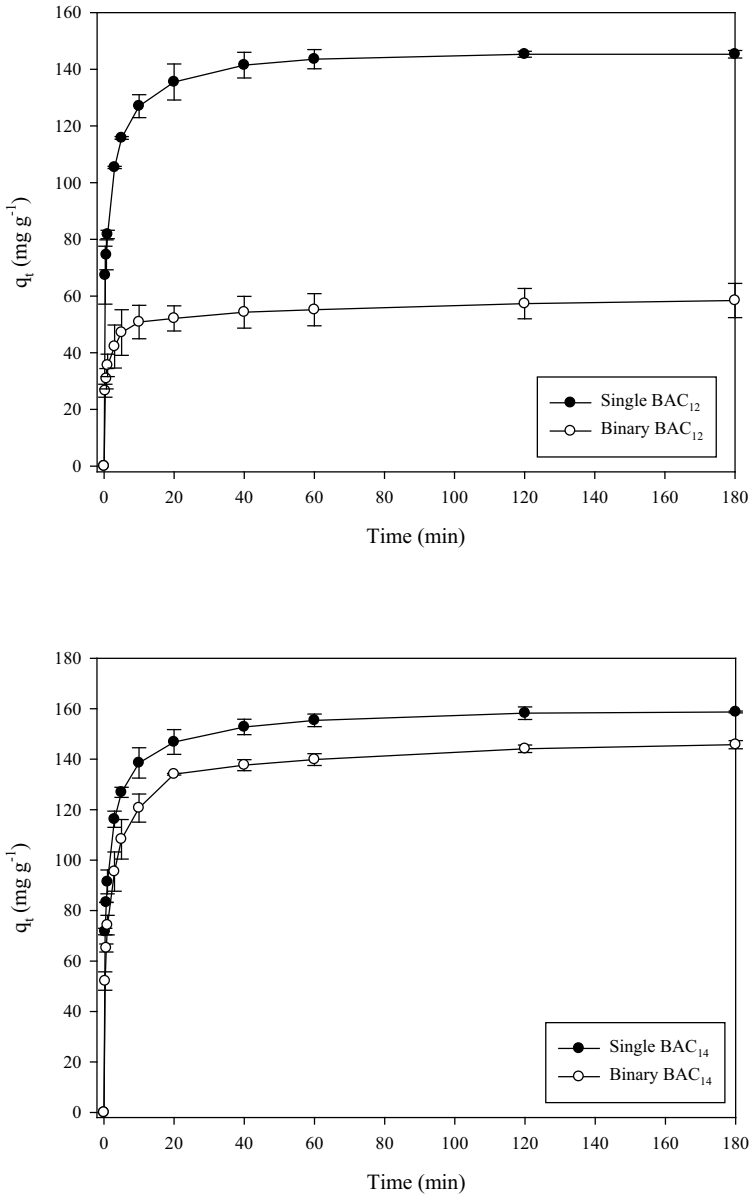


Figure 8. Comparison of (a) BAC_{12} and (b) BAC_{14} adsorption capacities of single BACs and binary BACs ($[C_0]$ = 200 mg L^{-1}; temperature = 25 °C; pH = 7.0 ± 0.1; contact time = 0–180 min; [PAC] = 1.2 g L^{-1})

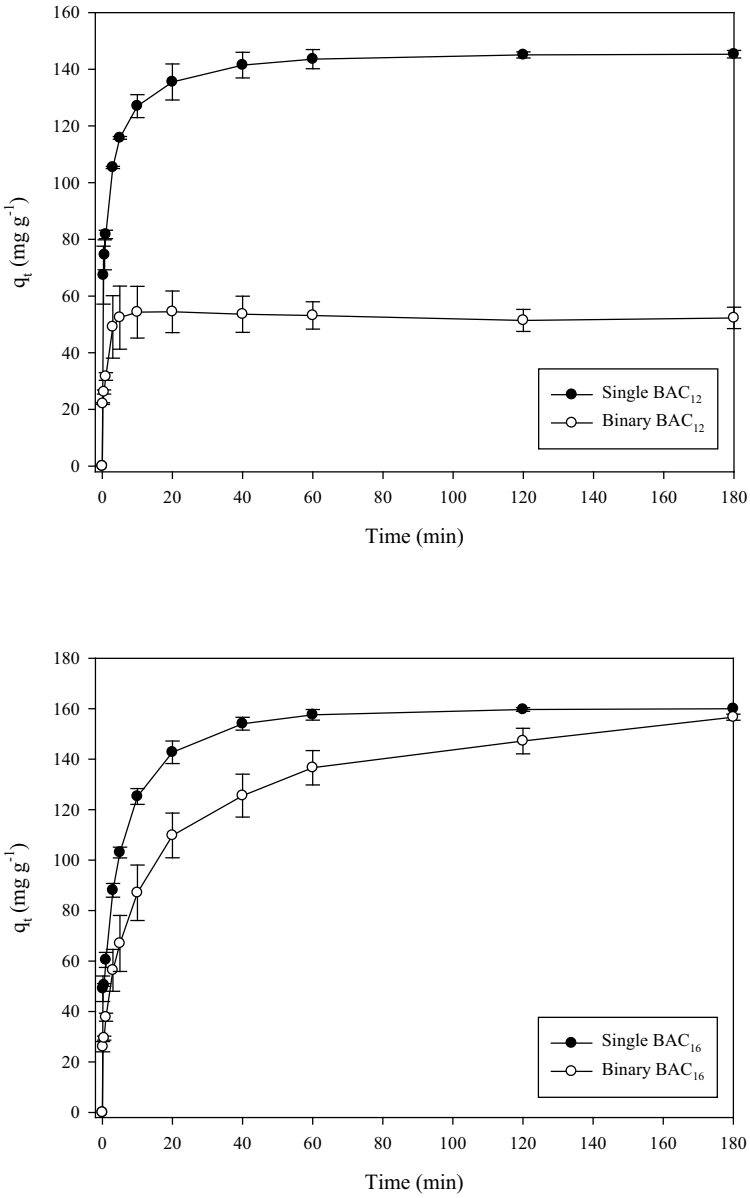


Figure 9. Comparison of (a) BAC_{12} and (b) BAC_{16} adsorption capacities of single BACs and binary BACs ($[C_0]$ = 200 mg L^{-1}; temperature = 25 °C; pH = 7.0 ± 0.1; contact time = 0–180 min; [PAC] = 1.2 g L^{-1})

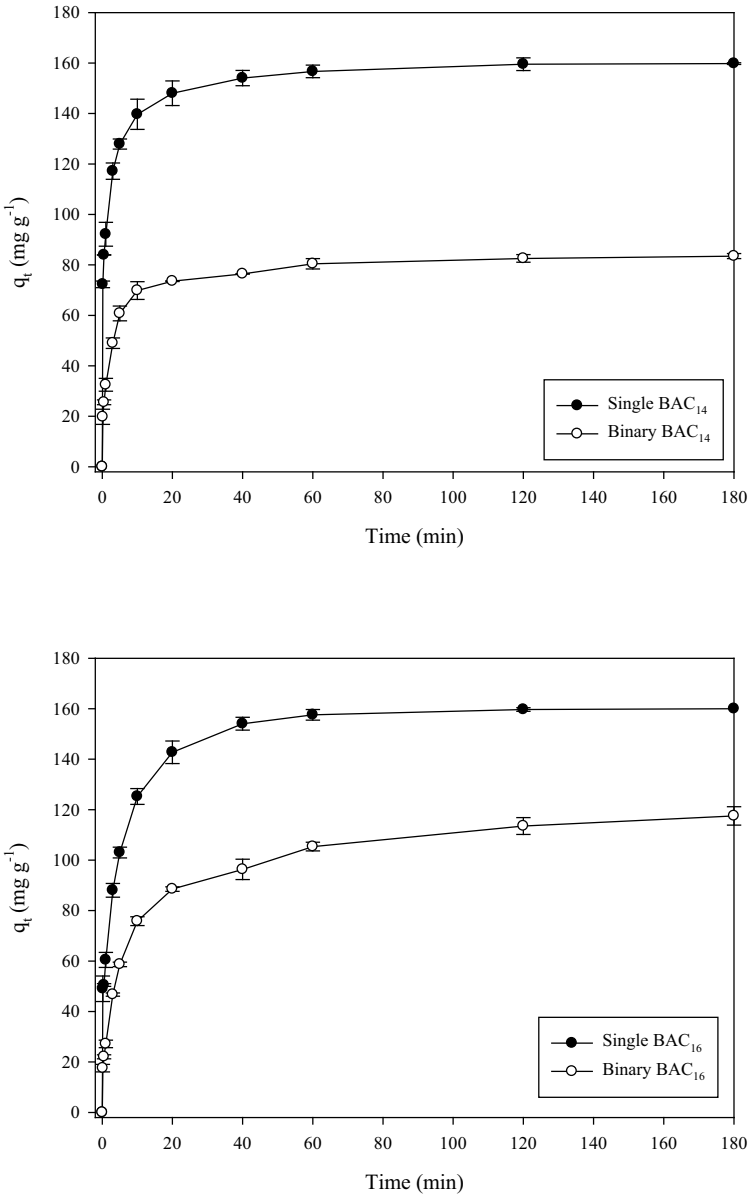


Figure 10. Comparison of (a) BAC_{14} and (b) BAC_{16} adsorption capacities of single BACs and binary BAC ($[C_0]$ = 200 mg L^{-1}; temperature = 25 °C; pH = 7.0 ± 0.1; contact time = 0–180 min; [PAC] = 1.2 g L^{-1})

From the results of the binary experiments, it explained that adsorption of PAC had more interaction between BAC_{16} than BAC_{12}. To confirm this, adsorption experiment was conducted in mixture of BAC_{12}, BAC_{14} and BAC_{16} ternary solution of 200 mg L^{-1} respectively. Figure 11 shows ternary solution of BAC_{12}, BAC_{14} and BAC_{16} adsorption onto PAC. Mixture of 3 different BACs adsorption results showed that the adsorption capacities of each of the BACs were decreased compared to single BAC experiment and also binary experiment results. BAC_{12} had the largest adsorption capacity reduction to 76.0 %, followed by BAC_{14} to 52.0 % and BAC_{16} had the smallest adsorption capacity reduction to 30.5 %. Similar result to the binary experiments, PAC had relatively stronger affinity for BAC_{16} than BAC_{12} and BAC_{14}. Because the interaction between PAC and BACs is mainly due to van der Waals interaction. Thus, BAC_{16}, which has a higher molecular weight, was able to have a stronger interaction on PAC than other BACs and to have a higher percentage of adsorption in mixture solution.

Another ratio of ternary solution experiment was performed. The ratio of the ternary solution that detected in nature environment was approximately 70 %, 20 % and 10 % (BAC_{12}, BAC_{14} and BAC_{16} respectively) (Li et al., 2014). Total concentration of BACs was 200 mg L^{-1} and other conditions of experiment were the same as binary solution experiments. The result was shown in Figure 12. As shown in Figure 12, BAC_{12} was decreased about 95.1 %, BAC_{14} and BAC_{16} were removed before 2 hours. Similar to the previous trend, BAC_{16} had high removal trend, followed by BAC_{14} and BAC_{12}.

Other binary solution (Dodecyl trimethyl ammonium chloride ($C_{12}TMA$) and BAC_{16}) experiment with using primary sludge, the adsorption capacities of $C_{12}TMA$ decreased to

37.0-52.5 %, but BAC_{16}, which had longer alkyl chain length than $C_{12}TMA$, slightly decreased to 0.4-4.3 % (Ismail et al., 2010). As a result of this experiment, mixture BACs will tend to be different from single BACs of mobility, overall fate and effect in water and sediment systems.

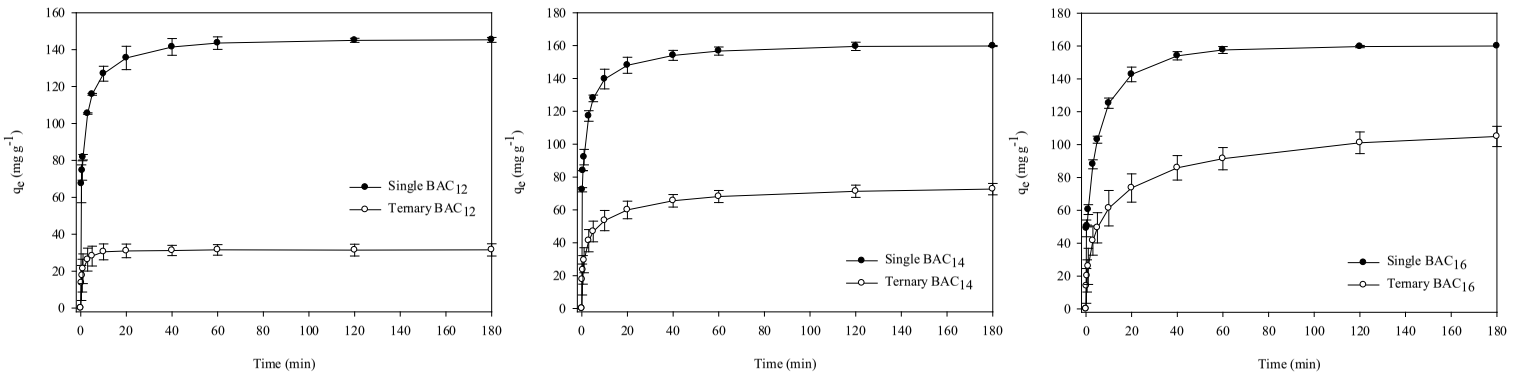


Figure 11. Comparison of (a) BAC_{12}, (b) BAC_{14} and (c) BAC_{16} adsorption capacities of single BACs and ternary BACs ($[C_0]$ = 200 mg L^{-1}; temperature = 25 °C; pH = 7.0 ± 0.1; contact time = 0–180 min; [PAC] = 1.2 g L^{-1})

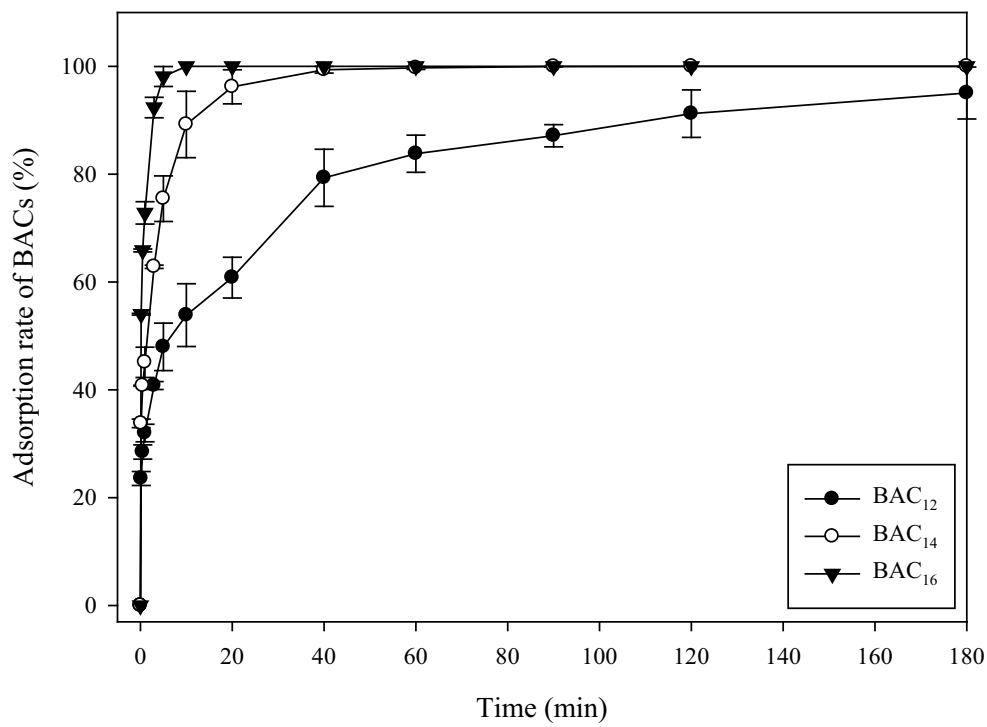


Figure 12. Comparison of BAC_{12} (140 mg L^{-1}), BAC_{14} (40 mg L^{-1}) and BAC_{16} (20 mg L^{-1}) adsorption rate of ternary BACs (temperature = 25 °C; pH = 7.0 ± 0.1; contact time = 0–180 min; [PAC] = 1.2 g L^{-1})

4. Conclusions

Adsorption of BAC_{12}, BAC_{14} and BAC_{16} from water was studied using PAC. Results showed that the BACs adsorption was dependent on pH, temperature and contact time. 200 mg L^{-1} of BAC_{12}, BAC_{14} and BAC_{16} were removed well to 90 % within 20 min. The kinetic studies revealed that BACs are quickly adsorbed onto PAC and BACs showed that the pseudo-second order reaction was more suitable than the pseudo-first order reaction. The adsorption equilibrium results showed that compared with Freundlich model and Langmuir model, Langmuir model was more suitable in adsorption of BAC ($R^2 > 0.99$). The effect of PAC adsorption on the pH range of 4-10 was verified that neutral and basic pH had better adsorption capacity than acidic pH. Adsorption capacity slightly decreased at basic pH because of OH^- attached to the micelle and had repulsive force between BACs and PAC. Thermodynamic analysis suggested that the adsorption process for BACs was spontaneous (ΔG^0: -3.931 ~ -5.641 kJ mol^{-1}) and endothermic (ΔH^0: 1.000 ~ 3.571 kJ mol^{-1}) in nature. ΔS^0 had positive value because of increasing randomness between BACs and PAC. In the presence of DOM, HA-BACs complexed could adsorb onto PAC and the removal rate of BACs were increased. The concentration of DOM was increased, the removal rate of BAC_{12}, BAC_{14} and BAC_{16} were also increased. In binary solution, mixture of BACs intercept each other and react differently from single solution. As a results of mixture solution of BACs experiments, adsorption of was increased in the order by PAC (BAC_{12} < BAC_{14} < BAC_{16}). The major reason is that the more alkyl chains, the better the adsorption due to the van der Waals interaction. It is expected that PAC could be suggested as sufficient

potential removal method for BACs from water treatment plants.

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국문초록

분말 활성탄을 이용한 benzalkonium chlorides (BACs) 흡착 제거에 대한 연구

최우석

서울대학교 보건대학원

환경보건학과 환경보건전공

4차 암모늄 (QACs)은 양이온 계면활성제로 화장품이나 세제용품같이 여러 산업제품으로 많이 쓰이고 있다. 그 중에서 염화 벤잘코늄 (BACs) 이라는 물질이 가장 많이 쓰이고 있으며 그 중에서 탄소사슬이 12개 있는 benzyl dimethyl dodecyl ammonium chloride (BAC_{12}), 탄소사슬이 14개 있는 benzyl dimethyl tetradecyl ammonium chloride (BAC_{14}), 탄소사슬이 16개

있는 Benzyl dimethyl hexadecyl ammonium chloride (BAC_{16})가 BACs 중에서 가장 많이 쓰이고 있다. BACs 또한 많은 산업용품 (식품, 섬유, 제지, 정유, 플라스틱 산업 등)으로 사용되고 관의 막힘이나 제품의 변질을 예방하는데도 쓰인다. BACs는 물이나 퇴적물 같은 환경 중에 검출이 되고 있고 소량으로도 독성이 존재한다. 하지만 일반적인 수처리시설로는 제거가 잘 이루어지고 있지 않다. 일반적인 방법이 아닌 고도산화처리 (AOP)나 흡착을 이용한 제거가 연구 되어있지만 실제 공정에 적용하기 어려운 연구도 있다. 이번 연구에서 BACs에 대한 기본적인 흡착 메커니즘을 조사해서 현실적으로 실제 처리장에 적용하기 쉬운 상용흡착제인 PAC를 이용해 주요한 BACs에 대해 제거하고자 한다. 흡착실험은 batch 형태로 했으며 BACs 측정은 HPLC를 이용해서 정량을 했다. PAC를 이용한 BAC 흡착특성에 대해서 알아 보기 위해 서로 다른 농도, pH, 온도로 실험을 했으며 BACs 혼합된 흡착과 단일 BACs에서의 어떤 흡착 차이가 있는지 확인했다. 실험 결과 BAC_{12}, BAC_{14}, BAC_{16} 모두 PAC에 흡착이 잘 되었으며 흡착 실험을 시작하고 20분에 90 % 이상 제거가 되었다. BACs의 흡착 kinetic은 pseudo-second (q_e : 144.93-161.29 mg g^{-1}, k_2 : 3.18 × 10^{-3}–9.16 × 10^{-3} g mg^{-1} min^{-1})을 따르고 isotherm은 Langmuir isotherm model (q_{max} = 188.68 – 206.19 mg g^{-1}, K_L : 4.89-8.10 L mg^{-1})에 더 적합했다. 여러 범위의 pH에서 흡착 실험을 해본 결과 산성 보다는 중성과 염기성에서 BACs 제거가 잘 되었다. 온도를 바꾸어 BACs 흡착 실험을 해본 결과 온도가 높을수록 잘 반응하는 흡열반응의 특징

을 가졌다. 수 중에 용존유기물이 존재하는 경우 BACs는 humic acids와 같은 용존유기물과 복합체를 형성하여, humic acid가 PAC에 흡착되는 경우 결과적으로 BACs의 제거율이 증가하는 것과 연결 된다. 서로 다른 BACs 두 가지를 동시에 흡착한 결과 BACs끼리 서로 경쟁 반응을 일어나서 단일 물질로 실험했을 때와 다른 특징을 보였다. 두 가지를 동시에 혼합해서 흡착한 결과, BACs 단일반응에 비해 2.1−66.7 %까지 흡착율이 감소했다. 2 가지 이상의 종류를 동시에 흡착해본 결과 BAC_{16}, BAC_{14}, BAC_{12} 순서로 흡착이 잘 되었다. BAC_{16}가 흡착이 더 잘 되는 이유는 탄소 사슬이 BAC_{12}, BAC_{14} 보다 많아서 van der Waals 힘이 더 크게 발생하여 PAC와의 서로 인력이 더 크게 발생했기 때문이다. 이 연구 결과를 통해 PAC를 이용한 BAC의 제거가 효과적인 방법이라 생각된다.

주요어: 흡착, BACs, 분말 활성탄, Kinetic, Isotherm, Binary solution

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